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REMARKS

Claims 8-13, 16-18, 47, 73 and 112 remain pending in the application after cancellation of previously pending claims 89-94. The Examiner has indicated that all claims have been rejected, although the Examiner indicates at p. 5 that claims 16-18 contain allowable subject matter subject to a provisional double patenting over pending claims 16-18 of Application No. 09/244,578.

I. Claim Rejections under 35 U.S.C. § 112

Claims 47 and 89-94 have been rejected for allegedly containing subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor, at the time the application was filed, had possession of the claimed invention. Claims 89-94 have been canceled, and so Applicant respectfully requests withdrawal of this rejection as it pertains to these claims.

With regard to claim 47, it is stated in the Office Action that "the specification is void of a written description which conveys that applicants had possession of the following subject matter as claimed: (A) "under deposition conditions effective to provide an outer aluminide layer region comprising a substantially single phase solid solution intermediate phase and an inner diffusion zone region proximate the substrate"; (B) "said intermediate phase including an average nickel concentration of about 50 to about 60% by weight so as to be nonstoichiometric relative to intermetallic compounds of aluminum and nickel, or aluminum and platinum, said outer aluminide layer region being substantially free of phase constituents other than said intermediate phase"; and (C) "oxidizing the diffusion aluminide layer under temperature and

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oxygen partial pressure conditions effective to form an alpha alumina layer." See Office Action at pp. 2-3.

There is no requirement that the subject matter of claim 47 be described literally in order to satisfy the written description requirement. See MPEP § 2163.02. Rather, claim limitations may be supported in the specification through "express, implicit or inherent disclosure." See MPEP § 2163(I)(B). The fundamental factual inquiry is whether the specification conveys with reasonable clarity to those skilled in the art that, as of the filing date sought, applicant was in possession of the invention as now claimed." Id. Applicant respectfully submits that the specification, as filed, conveys with reasonable clarity to those skilled in the art of aluminide, and platinum-aluminide, coatings on nickel-base superalloys that Applicant was in possession of the invention as now claimed, including these claim limitations of claim 47.

A. "An outer aluminide layer region with a solid solution intermediate phase and an inner diffusion zone region proximate the substrate"

Applicant previously argued that the limitation in claim 47 of an outer aluminide layer region with a solid solution intermediate phase and an inner diffusion zone region proximate the substrate would be reasonably conveyed to those skilled in the art from the specification as filed. In response, the Examiner has asserted that "there is no mention whatsoever, explicit or implied, of the above-specified claimed subject matter." See Office Action at p. 3. Further, the Examiner asserted in the Advisory Action mailed on November 26, 2002 that, "there is no description of a solid solution phase," and that figures 2A and 2B do not disclose an outer aluminide coating having a solid solution intermediate phase and an inner diffusion zone. See Advisory Action, Paper No. 17, at p. 2.

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In response, Applicant respectfully submits that the specification as filed includes a description of the process of forming the claimed diffusion aluminide layer. The specification expressly discloses that the claimed diffusion aluminide layer is formed by depositing a layer of platinum on the surface of a substrate (a nickel-base alloy); diffusing platinum from the layer of platinum into the substrate surface; providing a source of aluminum and diffusing aluminum from the source of aluminum into the substrate surface for a time sufficient to produce a surface region at the substrate surface. See Specification at p. 3, lines 16-22, p. 6, line 26 – p. 7, line 12. The specification provides further that platinum-aluminum protective surface regions have been known previously. Id. at line 28. The specification further expressly discloses that the platinum-aluminide region of the invention (34, 36 of Figs. 2A and 2B) is a single-phase composition of aluminum, platinum, nickel and the diffused components of the substrate, extending from the surface to a depth below the surface where the aluminum has decreased to 18 weight percent from the higher values closer to the surface. See Specification at p. 7, line 27 – p. 9, line 5. This region comprises β-NiAl, which is a phase of the binary nickel-aluminum system. See Specification at p. 8, line 21; USPN 5,716,710 at Fig. 2; col. 3, lines 14-15. Below 18 weight percent aluminum, the β-NiAl is not stable. See id. The β-NiAl comprises a solid solution of platinum and aluminide, as indicated by the use of the term "platinum-aluminide." See Specification at p. 7, line 28. Those skilled in the art know that aluminides are "ordered structures including aluminum and another metal." See USPN 5,238,752 at col. 2, lines 42-44. Thus, the specification conveys to one skilled in the art of aluminide, and platinum-aluminide, diffusion coatings that a diffusion coating prepared by the expressly stated method produces a solid solution phase of β-NiAl (or solid solution intermediate phase).

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Further, the Examiner has indicated that the specification has not conveyed to those skilled in the art that an inner diffusion zone would be created adjacent to both the solid solution intermediate phase (platinum-aluminide region 34, 36) and the substrate (32). However, those skilled in the art of aluminide, and platinum aluminide, diffusion coatings know that the weight gradient of the components of the diffusion zone created by the diffusion process continuously vary with depth from the surface of the platinum-aluminide region (or solid solution intermediate phase) some distance into the substrate adjacent to the platinum-aluminide region (or solid solution intermediate phase). That is, through the process of diffusion, the components that diffuse to create the platinum-aluminide region 34, 36 (or solid solution intermediate phase) would not simply create a β-NiAl platinum-aluminide region (or solid solution intermediate phase) having the claimed weight compositions of at least 18 weight percent aluminum, and then at the surface of the substrate suddenly revert to the substrate composition.

From the specification as filed, those skilled in the art of platinum-aluminide diffusion coatings would know that, adjacent to the platinum-aluminide region 34, 36 having a composition of 18 weight percent aluminum and 18 weight percent platinum, the substrate surface 32 adjacent to the platinum aluminide region 34, 36 would not comprise approximately 6 weight percent aluminum and no platinum, as found in the substrate compositions. See Specification at p. 6, lines 1-10. Rather, the process of diffusion would be known to those skilled in the art to create an inner diffusion zone in an area adjacent to the platinum-aluminide regions 34, 36 (or solid solution intermediate phase) and the substrate 32 that does not comprise β-NiAl, and yet does not comprise the composition of the substrate.

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The process of diffusion is explained in the Goward/Boone/Giggins reference, "Formation and Degradation Mechanisms of Aluminide Coatings on Nickel-Base Superalloys," previously submitted for support in the Amendment after Final Rejection dated November 13, 2002. See, for example, Fig. 6 (depicting approximate composition of various components by distance from the surface, and showing continuity of change in composition with increasing depth); Fig. 14. See also p. 239 (same mechanisms apply for different coating processes, as pack cementation, hot dipping, slurry methods, vapor deposition (both chemical and physical), fused salt electrolyte, flame or plasma spraying etc.) G.M. Kim, N.M. Yanar, E.N, Hewitt, F.S. Pettit, and G.H. Meier analyzed a single phase (Ni, Pt) Al coating made by GE according to the disclosed process. See "The effect of the type of thermal exposure on the durability of thermal barrier coatings," Scripta Materialia, 46 (2002) 489-495 (attached as Exh. A). Fig. 3 clearly shows an inner diffusion zone located between the platinum-aluminide region, and the substrate. See also Conner, ASTM article, at Fig. 1 and USPN 5,856,027 at Figs. 1, 3 (photographs showing an inner diffusion zone located between the outer platinum-aluminide region and the substrate).

Additionally, see J.H. Wood and E.H. Goldman, Chapter 13: "Protective Coatings," in Superalloys II, C.T. Sims, N.S. Stoloff and W.C. Hagel, eds., John Wiley and Sons, New York (1987) at pp. 359-384 (attached as Exh. B). See Fig. 1 at p. 361 and explanation at pp. 361-62, describing and illustrating a coating structure of the type produced in a low activity diffusion process in the temperature range disclosed in the specification such as that used to create single phase (Ni, Pt) Al coatings on superalloys. Fig. 1 clearly shows an inner diffusion zone between

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the outermost additive layer (the β-NiAl phase) and the superalloy. On p. 362, the text expressly describes an "'interdiffusion zone' between the outer layer and the substrate."

Thus, the specification as filed would have conveyed to one skilled in the art of aluminide, and platinum-aluminide coatings, that there would be region (an "inner diffusion zone") between the platinum-aluminide region 34, 36 (or solid solution intermediate phase) and the substrate 32.

B. "Said intermediate phase including an average nickel concentration of about 50 to about 60% by weight so as to be nonstoichiometric relative to intermetallic compounds of aluminum and nickel, or aluminum and platinum, said outer aluminide layer region being substantially free of phase constituents other than said intermediate phase"

Applicant submits that the original application as filed also conveys to one skilled in the art of platinum-aluminide diffusion coatings the limitation of claim 47 of the platinum-aluminide region (intermediate phase) having "an average nickel concentration of about 50 to about 60 % by weight." Applicant previously argued that aluminide diffusion coatings include Ni concentrations at a higher level than the relative Ni concentration in the alloy substrate due to the preferential outward migration of Ni as compared to the other alloy components to form the remainder of the composition of the diffusion coating. Based on the weight percent nickel in the expressly disclosed nickel-base superalloy substrates of 48 wt. % (RN6); 63 wt. % (RN5); and 69 wt. %, Ni would constitute from 36 wt. % on RN6 substrate; to 47 wt.% on RN 5 substrate; to 51 wt. % of the platinum-aluminide region composition on the substrate of claims 7(c) and 13(c). Since Ni *preferentially* migrates out of the alloy substrate into the diffusion layer at *higher* rates than the other alloy substrate components, those skilled in the art of aluminide, and platinum aluminide, diffusion coatings would know that the Ni concentration in the diffusion coating will

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exceed 36 wt. % on RN6 substrate; 47 wt.% on RN 5 substrate; and 51 wt. % of the platinum-aluminide region composition on the substrate of claims 7(c) and 13(c).

The Examiner asserted that Applicant's argument was not convincing because the Ni concentrations "would clearly depend upon the processing conditions used to make the coatings which applicant's claims have broad variations, the amounts calculated by applicants do not support the 50 to 60 % . . . range . . . claimed." See Advisory Action at p. 2. G.M. Kim, N.M. Yanar, E.N, Hewitt, F.S. Pettit, and G.H. Meier analyzed a single phase (Ni, Pt) Al coating on RN5 substrate made by GE according to the disclosed process. See Exh. A. This analysis shows composition gradients of atomic % (38-48 Al) – (40-48 Ni) – (5-12 Pt) – (5 Cr) – (5 Co). Within this range, a composition of Ni-44 Al-5 Cr-5 Co-5 Pt (atomic) is equivalent to 50.3 Ni-20 Al-4.95 Cr-5.61 Co-18.6 Pt, by weight. Thus, the weight range of 50-60 weight % Ni, for platinum-aluminide diffusion coatings prepared as disclosed in the specification, have been actually reduced to practice and would inherently be formed on an RN5 substrate by the disclosed process. This supports Applicant's argument that the Ni present in the diffusion coating, under the disclosed process conditions, exceeds the relative Ni concentration by weight in the substrate. That is, the Ni preferentially migrates into the diffusion zone over other substrate constituents.

The Examiner repeated the grounds for his rejection of the "nonstoichiometric" limitation as presented in page 8 of the Final Rejection dated May 15, 2002. See Advisory Action at p. 2. Here, the Examiner stated that "the nickel range is . . . very speculative and makes many unfounded assumptions . . . the discussion with respect to 'nonstoichiometric' . . . is . . . equally speculative and unsupported by factual evidence." See Final Rejection at p. 8. Here, Applicant has presented factual, published evidence that the Ni weight in the claimed platinum-aluminide

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diffusion coating exceeds 50 weight %. Thus, now that this point is factually supported, the calculations presented on nonstoichiometry found on pages 10-11 of the Amendment and Response dated April 3, 2002 show necessarily that Al is hypostoichiometric in a β-NiAl structure having over 50 weight % Ni.

Here, Applicant has claimed Ni in the platinum aluminide region at about 50 to about 60 wt. %. Given the factual support of more than 50 weight % of Ni, Applicant respectfully requests that the rejection under 35 U.S.C. § 112, first paragraph for failure to provide support for the claimed Ni wt. concentration of about 50 to about 60 wt. % be withdrawn.

C. "Oxidizing the diffusion aluminide layer under temperature and oxygen partial pressure conditions effective to form an alpha alumina layer"

Finally, it is stated that the limitation in claim 47 of "oxidizing the diffusion aluminide layer under temperature and oxygen partial pressure conditions effective to form an alpha alumina layer" is totally lacking support in the application as filed. Applicant previously argued that oxidation of the surface of a platinum-aluminide layer to provide a protective aluminum oxide scale prior to addition of a ceramic layer in a thermal barrier coating system is well known in the art; that the formation of an alumina layer prior to depositing a ceramic layer has long been known to greatly improve adherence of the ceramic layer to the bond coat in thermal barrier coating systems; and that sufficient oxygen is available in the annealing process to form an alumina layer from the aluminum on the surface of the protective coating under the temperature and time conditions given in the application. See Amendment after Final Rejection, November 15, 2002, at pp. 18-19.

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The Examiner asserted that the "specification describes no formation of an alpha alumina layer by oxidizing the diffusion aluminide layer under temperature and oxygen partial pressure conditions effective to form an alpha alumina layer." See Advisory Action at p. 2. In so doing, the Examiner restated the positions set forth in the Final Rejection of May 15, 2002. Id. There, the Examiner asserted that, "to say that the substrate is annealed with absolutely no indication of providing an oxidizing atmosphere or formation of oxide is not an oxidizing step." See Final Rejection at p. 8.

In response, Applicant respectfully notes that aluminum easily combines with oxygen to form alumina even at very low partial pressures of oxygen. For example, Ellingham diagrams are used to show the formation potential for compounds relative to oxygen potentials and temperatures. One such diagram is attached as Exh. C. A copy of this diagram may be found at D.R. Gaskell, Introduction to Metallurgical Thermodynamics, Second Edition, Hemispherical Publishing Corporation, New York (1981) at p. 287. The partial pressure of oxygen required for alumina to be formed on aluminum or an aluminum-containing coating, such as the platinum-aluminide coating of the invention, at 1975°F is 10^{-30} to 10^{-34} atm. Typical annealing conditions known to those skilled in this art comprise a vacuum heat treatment at 10^{-5} torr. This atmosphere contains 2.6×10^{-9} atm oxygen, which according to the Ellingham diagram is more than sufficient oxygen to form alumina.

In addition, it is known to those skilled in the art that an alumina layer will form on an aluminide coating during preheating of the surface prior to deposition of the ceramic layer. See USPN 5,238,752 at col. 6, lines 55-59. Claim 47 includes the deposition of a ceramic thermal barrier layer and therefore will necessarily include a preheating step of the surface. It is known

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to those skilled in the art that the layer of alumina needed for adherence of the ceramic layer is very thin, and forms upon heating, and that "a separate step of oxidation is not normally required . . . [t]he oxidation occurs during normal preheating of the coated substrate prior to deposition of the ceramic topcoat." See USPN 5,238,752 at col. 6, lines 45-50; lines 55-59. Applicant thus respectfully submits that the specification as filed would convey to one skilled in the art of platinum-aluminide diffusion coatings having deposited ceramic thermal barrier layers that an alumina layer would form on the aluminide coating of the invention during at least the preheating stage prior to the ceramic thermal barrier layer deposition.

For all the reasons set forth above, Applicant respectfully requests the withdrawal of the claim rejections under 35 U.S.C. § 112, first paragraph and to allow claim 47.

II. Claim Rejections Under 35 U.S.C. § 102(b)

Claim 8 is rejected under 36 U.S.C. § 102(b) as allegedly anticipated by Conner et. al. (ASME article). The Examiner asserts that Conner discloses the CVD PtAl process at pages 2 and 5 and the representation in Fig. 3 for the "CVD PLATINUM ALUMINIDE." See Office Action at p. 3.

Applicant respectfully submits that Conner does not disclose each and every limitation of claim 8, and therefore does not anticipate claim 8. Specifically, claim 8 is a method claim for preparing an article having a platinum-aluminide surface region. The 2d and 3d limitations of claim 8 provide that a layer of platinum is deposited on a substrate surface, and thereafter the platinum is diffused from the layer of platinum into the substrate surface. Thereafter, a source of aluminum is provided. Conner at pages 2 and 5 and Fig. 3 does not disclose these process steps. Rather, Conner discloses at p. 2 only that the tested platinum aluminide coatings were produced

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using pack processes and were given post-coat heat treatment at 1925°F to "ductilize the coatings and to complete alloy heat treatment requirements." There is no disclosure at all of process steps at p. 5 or Fig. 3. Rather, Fig. 3 illustrates only the weight percents of the coating constituents as a function of depth from the surface of the coatings.

Since the cited sections of Conner do not disclose each and every step of claim 8, Applicant respectfully submits that Conner does not anticipate claim 8 and asks that this rejection be withdrawn.

III. Claim Rejections Under 35 U.S.C. § 103

Claims 9, 10, 11, 12, 13, 73 and 112 have been rejected under 35 U.S.C. § 103(a). See Office Action at pp. 4-5. The Examiner asserts that claim 11 is obvious over Conner; that claims 9, 10, 73 and 112 are obvious over Conner in view of Duderstadt, USPN 5,238,752 ("Duderstadt"); and that claims 12 and 13 are obvious over Conner in view of Wukusick, USPN 5,100,484 ("Wukusick).

A. Claim 11 is Rejected as Allegedly Obvious Over Conner

The Examiner asserts that, based on the Conner disclosure, "it would have been obvious to have derived the amounts of Pt in the range of claim 11 through routine experimentation to optimize the corrosion resistance of the coating." See Office Action at p. 4. However, claim 11 is dependent on claim 8 and therefore incorporates the claim limitations of claim 8. Since Conner does not disclose each and every process limitation of claim 8 as discussed in Section II above, Conner does not disclose each and every limitation of claim 11. Therefore, Conner does not support a *prima facie* case of obviousness for claim 11.

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B. Claims 9, 10, 73 and 112 Are Rejected As Allegedly Obvious Over Conner in view of Duderstadt

The Examiner asserts that claims 9, 10, 73 and 112 are allegedly obvious over Conner in view of Duderstadt. See Office Action at p. 4. However, claims 9 and 10 are dependent on claim 8, and as discussed Conner does not disclose each process limitation of claim 8 including the steps of depositing platinum on a substrate, diffusing the platinum into the substrate and thereafter providing a source of aluminum. Duderstadt likewise does not disclose these steps. Since Conner and Duderstadt in combination do not disclose each and every step of claim 8. these references do not form a *prima facie* case of obviousness of claims 9 and 10.

Claims 73 and 112 are also not rendered obvious by a combination of Conner and Duderstadt. Claim 73, from which claim 112 depends, claims a method of forming a thermal barrier coating on a substrate wherein the aluminum content and the platinum content are relatively high adjacent to the surface and decrease with increasing depth into the aluminide layer and the substrate. In contrast, Conner discloses only a platinum aluminide coating wherein the platinum increases with increasing depth into the surface before it begins decreasing. See Fig. 3 (MDC-150 on SC Alloy). Duderstadt likewise does not disclose a coating where the aluminum content and the platinum content are relatively high adjacent to the surface and decrease with increasing depth into the aluminide layer and the substrate. Finally, neither Duderstadt nor Conner discloses the weight % ranges of Pt and Al set forth in claim 73. Claim 73 recites a Pt concentration from about 8 to about 45 wt. %, and Al from about 18 to about 28 wt. %. In contrast, Duderstadt has no disclosure on the composition of the platinum aluminide

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coating in terms of wt.% Pt or Al, and none of the examples in Conner disclose Pt concentration up to 45 wt. %.

Thus, Conner and Duderstadt in combination do not disclose each and every limitation of claims 73 and 112, and therefore do not form a *prima facie* case of obviousness of claims 73 and 112.

C. Claims 12 and 13 are Rejected as Allegedly Obvious over Conner in View of Wukusick

Finally, claims 12 and 13 have been rejected as allegedly obvious over Conner in view of Wukusick. See Office Action at p. 5. Claims 12 and 13 are dependent from claim 8. As discussed, Conner does not disclose each process limitation of claim 8 including the steps of depositing platinum on a substrate, diffusing the platinum into the substrate and then providing a source of aluminum. Wukusick likewise does not disclose these steps. Since Conner and Wukusick in combination do not disclose each and every step of claim 8, these references do not form a *prima facie* case of obviousness of claims 12 and 13.

Applicant respectfully submits that these references, alone or in combination, do not disclose each and every limitation of the rejected claims and therefore that these rejections should be withdrawn.

IV. Double Patenting Rejection

Claims 8-13, 16-18 and 89-94 have been provisionally rejected under 35 U.S.C. § 101 as claiming the same invention as that of claims 8-13 and 16-18 and 87-92 of copending Application No. 09/244,578. Claims 47, 73 and 112 are provisionally rejected under the

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judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 47, 71, and 110 of copending application Ser. No. 09/244,578.

Applicant acknowledges this rejection, and will amend or cancel claims 8-13 and 16-18 or file a terminal disclaimer pursuant to 37 C.F.R. § 1.321(c) for claims 47, 73 and 112 if this rejection is appropriate at that time. The rejections corresponding to claims 89-94 are moot in light of the cancellation of these claims.

CONCLUSION

Applicant submits that the application is in condition for allowance and respectfully requests entry of this amendment and a notice of allowance for all the pending claims. Should the Examiner determine that any further action is necessary to place this application in condition for allowance, the Examiner is kindly requested and encouraged to telephone Applicant's undersigned representative at the number listed below.

Applicant authorizes the fee of $950.00 for a three month extension of time to be deducted from Deposit Account No. 50-0206. If any variation is found between the amount authorized to be charged and the amount due, please credit or deduct the difference from the undersigned's Deposit Account No. 50-0206.

Respectfully submitted,

HUNTON & WILLIAMS

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The effect of the type of thermal exposure on the durability of thermal barrier coatings

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Abstract

The effect of cycle frequency on the spallation failure of thermal barrier coatings has been investigated. The exposure conditions affect the lifetimes of the coatings and can even change the relative performance of different bond coats. The very strong effect of exposure temperature is consistent with thermally grown oxide growth being a first order variable in scale failure. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Oxidation; Thermal barrier coating; Thermal cycling

1. Introduction

The major factor controlling the life of thermal barrier coatings (TBCs) is the resistance of the coating to spallation under the influence of stresses generated during thermal exposure [1,2]. Typical TBC systems consist of a series of layers. A Ni-base superalloy substrate is coated with an Al-rich bond coat (either a diffusion aluminide or NiCoCrAl Y overlay coating) onto which is deposited a yttria-stabilized zirconia (YSZ) topcoat. During fabrication and service a thermally grown oxide (TGO) forms between the bond coat and the YSZ. Ideally the TGO is pure α-alumina but oxides of other components have also been observed to form [1]. High temperature exposure results in growth of the TGO and sintering of the YSZ, both of which increase the elastic energy stored in the system after cooling to room temperature. Exposure also leads to microstructural and/or chemical changes, which result in regions of decreased fracture toughness. Eventually, fracture initiates and propagates through one or more of the following: the YSZ, the TGO, the interface between the TGO and bond coat or between the TGO and YSZ. A number of studies of TBC degradation have indicated that the fabrication method of the YSZ and bond coat can influence the crack path and the time to failure [3]. However, different results are often obtained by different investigators studying nominally identical coatings. It has been suggested that these differences arise from variations in the exposure conditions [4]. This paper presents the results of a study to evaluate the effects of the type of thermal exposure on TBC

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failure for two TBC systems: one with platinum-modified diffusion aluminide bond coats and the other with NiCoCrAlY bond coats.

2. Experimental

TBCs of YSZ (8 wt.% yttria) were deposited by electron beam physical vapor deposition on one face and the periphery of 25.4 mm diameter, 3.2 mm thick, bond-coated disks of the single crystal nickel-base superalloy René N5. The Pt–aluminide bond coats were prepared by electroplating a thin (5–7 μm) layer of platinum on the substrate, aluminizing in a CVD reactor, and grit blasting with alumina grit. The composition of the bond coat varied slightly across the thickness but was in the range in at.% (38–48 Al)–(40–48 Ni)–(5–12 Pt)–(5 Cr)–(5 Co). The NiCoCrAlY bond coats were prepared by a plasma spray process (A) and a detonation process (B) and had the approximate composition in at.% 24Al–41Ni–19Co–15Cr–0.1Y. After coating deposition the NiCoCrAlY coatings were vacuum heat treated, peened with steel shot, and vibratory finished with alumina media. At this point the surface roughness was 1.5 μm R_a. Prior to TBC deposition, the bond coat surface was grit blasted to 1.8–2.0 μm R_a. Significant performance differences were not observed in this investigation between NiCoCrAlYA and B. Consequently, the results will be presented for both bond coats as NiCoCrAlY.

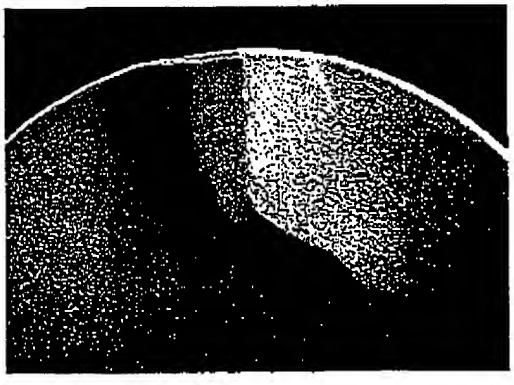

Fig. 1. Macroscopic photograph of a failed TBC specimen.

The specimens were exposed in laboratory air at temperatures of 1000, 1100 and 1200 °C under either isothermal or cyclic conditions. Many of the cyclic exposures were performed in vertical tube furnaces, which were modified to contain a large thermal mass, which permitted rapid specimen heating, and fitted with a high velocity air blower, which permitted rapid specimen cooling. Three thermal cycles were used with these furnaces as follows:

A: Heat to 1100 °C in 2.5 min, hold at 1100 °C for 5 min, cool to 30 °C in 2.5 min.
B: Heat to 1100 °C in 2.5 min, hold at 1100 °C for 55 min, cool to 35 °C in 2.5 min.
C: Heat to 1100 °C in 2.5 min, hold at 1100 °C for 39.5 min, cool to 210 °C in 18 min.

Additional experiments were performed in a commercial bottom-loading furnace (CM furnaces). The thermal cycle was similar to Cycle B above except that every 20 cycles the specimens were removed and kept in a desiccator for several hours, examined, and reinserted into the furnace. The restart involved heating to the oxidation temperature in 20 min.

Failure of the specimens was taken to be a measurable amount of separation of the TBC from the face of the specimen. A macroscopic photograph of a typical failure is presented in Fig. 1.

3. Results and discussion

A typical as-processed microstructure for the NiCoCrAlY bond coats is presented in Fig. 2. The 150 μm thick coating consisted of two phases: β-NiAl and γ-solid solution. (volume fraction of β ≈63%). Embedded grit particles were observed at the coating/substrate interface and at the TBC/coating interface. Smaller oxide particles and a few small pores were observed throughout the coating. Fig. 3 presents a typical as-processed microstructure for the platinum aluminide bond coat. The 50 μm thick coating consisted of single phase β-NiAl with Pt and various substrate elements in solution. Embedded alumina grit particles were observed at

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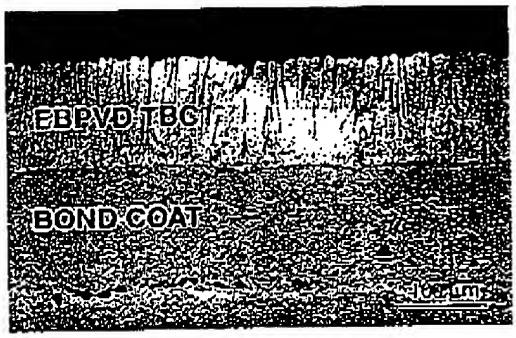

Fig. 2. Cross-section micrograph showing an as-processed TBC with NiCoCrAlY bond coat.

Fig. 3. Cross-section micrograph showing an as-processed TBC with Pt–aluminide bond coat.

the original superalloy substrate surface and occasionally at the TBC/coating interface.

The times to failure for the various thermal exposures are presented in Table 1. Several observations can be made from these results:

1. Isothermal exposures and one-hour cycles in the bottom-loading furnace give similar hot-times to failure at both 1100 and 1200 °C.
2. Each increase in T_H by 100 °C decreases the hot-time to failure by about a factor of 10 for both isothermal exposure and one-hour cycles in the bottom-loading furnace.
3. Increasing cycle frequency from 1/h (Cycle B) to 6/h (Cycle A) *decreases* the hot-time to failure by about a factor of 2 but *increases* the number of cycles to failure by about a factor of 4 for the Pt–aluminide bond coats.
4. Increasing cycle frequency from 1/h (Cycle B) to 6/h (Cycle A) *increases* the hot-time to failure by about a factor of 2 and *increases* the number of cycles to failure by more than a factor of 10 for the NiCoCrAlY bond coats.
5. Maintaining the bottom temperature of the cycle T_L at 210 °C (Cycle C) rather than 35 °C (Cycle B) increased the hot-time to failure of the NiCoCrAlY bond coats by about a factor of two and for the platinum aluminide bond coats by about 30%.

The type of thermal exposure not only affected the time to failure but also the fracture path when the specimens failed. Fig. 4 presents the surface morphology and microstructure of a NiCoCrAlY bond coat after failing during one-hour cycles

Table 1
Average failure times for TBCs with Pt–aluminide bond coats and NiCoCrAlY bond coats with different thermal exposures

Type of exposure	Pt-Al		NiCoCrAlY	
	Cycles	Hot-time (h)	Cycles	Hot-time (h)
T_H = 1000 °C, one-hour cycles bottom-loading furnace	NA	NA	670 (2)	559 (2)
1100 °C, isothermal	–	1000 (2)		<100 (2)
T_H = 1100 °C, one-hour Cycle B ($T_L \approx 35$ °C)	1570 (2)	1440 (2)	232 (4)	213 (4)
T_H = 1100 °C, 10 min Cycle A ($T_L \approx 30$ °C)	5422 (2)	452 (2)	5785 (2)	483 (2)
T_H = 1100 °C, one-hour Cycle C ($T_L \approx 210$ °C)	2403 (1)	1582 (1)	833 (2)	549 (2)
T_H = 1100 °C, one-hour cycles bottom-loading furnace	1168 (3)	974 (3)	87 (6)	72 (6)
1200 °C, isothermal	–	100 (2)	–	NA
T_H = 1200 °C, one-hour cycles bottom-loading furnace	128 (3)	107 (3)	7 (2)	6 (2)

Parentheses indicate the number of specimens tested; T_H is the temperature of the high temperature hold; T_L is the minimum temperature during the cooling part of the cycle.

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Fig. 4. Surface (a) and cross-section (b) of a TBC with a NiCoCrAlY bond coat after failure under Cycle B conditions.

from 1100 °C (Cycle B). The fracture progressed primarily along the TGO/bond coat interface, Fig. 4a (image analysis indicated 74% exposed bond coat) with excursions into the TGO. This behavior has been described previously [5,6] and explained as fracture initiating at defects, such as transient oxides or pockets of reactive element rich oxides but then propagating along the interface to release all of the elastic energy stored in the TGO. A similar mechanism has been proposed for the failure of TBCs with EB-PVD NiCoCrAlY bond coats [7]. A cross-section of this specimen (Fig. 4b) indicated the bond coat thickness had decreased uniformly by about 10%. An Al-depleted layer was present at the bond coat TGO interface and the overall volume fraction of β had decreased from 63% to 34%. This is consistent with the decreased coating thickness as γ has a smaller molar volume than β. This cross-section also shows several areas where internal oxidation of reactive elements has occurred.

Fig. 5 presents the surface morphology and microstructure of the NiCoCrAlY bond coat after failure during rapid cycling from 1100 °C (Cycle A). The fracture surface (Fig. 5a) is qualitatively similar to that for the one-hour cycles (≈70% exposed bond coat) except that there are a few unoxidized voids on the bond coat surface. The cross-section of this specimen (Fig. 5b) shows that the coating thickness has decreased to about 135 μm and the β phase has retreated from the TGO/bond coat interface and the coating/substrate interface. In some locations oxidation penetrated nearly through the coating. The TGO contained reactive element oxides and spinel was present between the TGO and TBC in some locations (Fig. 5c). However, there were no substantial differences between this TGO and the one formed during one-hour cycles. Given the similarities in the degradation microstructures, it is difficult to explain why the hot-time to failure increases for this bond coat when the cycle frequency is increased. One might speculate that some sources of stress relief are more effective during rapid cycling.

Fig. 6 presents the degradation microstructure of one of the Pt–aluminide bond coats after failing during one-hour cycles from 1100 °C (bottom-loading furnace). The fracture has progressed mainly in the TGO and TBC, presumably as a result of ratcheting of the TGO. The development of this morphology on Pt–aluminide bond coats has been described by Mumm and Evans [8] and a model has been developed for the formation of ratchets [9]. This model invokes plastic deformation of the bond coat as a major contributor to ratcheting. The cross-section of the coating indicates γ′ formation at β grain boundaries and the relative absence of voids in the bond coat. The β to γ′ transformation and the consequent decrease in molar volume has been proposed as an alternative cause of ratcheting [10].

Fig. 7 presents the degradation microstructure of one of the Pt–aluminide bond coats after failure during rapid cycling from 1100 °C (Cycle A). The fracture surface (Fig. 7a) indicated substantial amounts of failure in the TGO and TBC (≈25%

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Fig. 5. Surface (a) and cross-sections (b, c) of a TBC with a NiCoCrAlY bond coat after failure under Cycle A conditions.

Fig. 6. Surface (a) and cross-section (b) of a TBC with a Pt–aluminide bond coat after failure during one-hour cycles in the bottom-loading furnace.

exposed bond coat). The bond coat had rumpled and voids were present on the bond coat surface (black arrow). Cross-sections of this specimen (Fig. 7b and c) indicate extensive void formation at the TGO/bond coat interface. The surfaces of some of the voids have been oxidized as the result of fracture of the overlying oxide while others remained unoxidized. Large voids were also formed in the bond coat near the bond coat/substrate interface. Such voids have been proposed to result from the β to γ′ transformation [10]. However, the large voids formed with rapid cycling and the absence of voids with one-hour cycles, even though there was more γ′ formation in the latter case,

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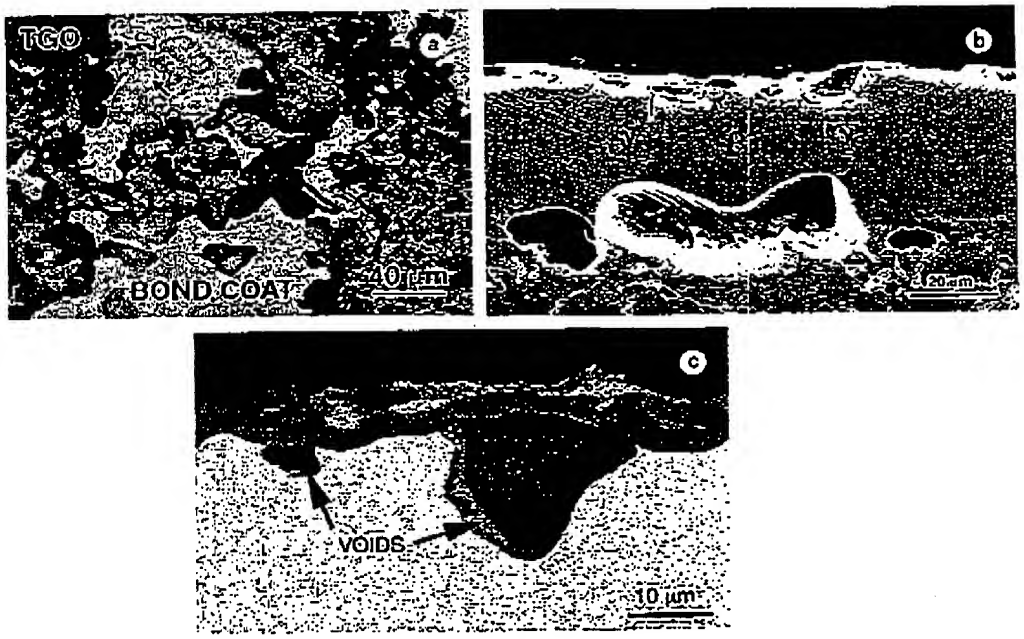

Fig. 7. Surface (a) and cross-sections (b, c) of a TBC with a Pt–aluminide bond coat after failure under Cycle A conditions.

suggest that plastic deformation of the bond coat is a major contributing factor to the void formation. These voids were often in contact with strips of γ' extending down from the TGO/bond coat interface. The extensive void formation, particularly at the TGO/bond coat interface, is believed to be responsible for the decreased hot-time to failure of the Pt–aluminide bond coat under rapid cycling conditions.

The strong effect of oxidation temperature on failure time indicates that TGO growth rate, i.e. oxide thickness, is a key factor in determining TBC failure. Tolpygo and Clarke [11] argue that there is a critical oxide thickness (5–7 μm for Pt–aluminide bond coats) beyond which the coating will fail. Wright [12] questions the validity of the "critical oxide thickness". The effect of temperature and similar failure times for isothermal and one-hour cycling observed in this study and [11] support the concept of a critical oxide thickness for failure. However, coatings can fail at smaller oxide thicknesses if other processes intervene, e.g. the interface voiding observed when the Pt–aluminide bond coats were rapidly cycled.

4. Summary and conclusions

The above results show clearly that the exposure conditions used for thermal cycling TBC systems affect the lifetimes of the coatings and can even change the relative performance of different bond coats. The very strong effect of exposure temperature is consistent with TGO growth being a first order variable in scale failure, but it is important to emphasize that, under some test conditions, other factors assume a major role in determining failure times.

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SUPERALLOYS II

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Chapter 13

Protective Coatings

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A coating for use at high temperatures on a superalloy substrate can be defined as a surface layer of material, either ceramic or metallic or combinations thereof, that is capable of precluding or inhibiting direct interaction between the substrate and a potentially damaging environment. This damage can either be metal recession due to oxidation/corrosion or a reduction in substrate mechanical properties due to the diffusion of harmful species into the alloy at high temperature. Coatings used on superalloys do not function as inert barriers. Rather, they provide protection by interacting with oxygen in the environment to form dense, tightly adherent oxide scales that inhibit the diffusion of damaging species such as oxygen, nitrogen, and sulfur into the substrate. Coatings must therefore be rich in those elements (such as Al, Cr, or Si) that readily participate in the formation of these protective scales. Essentially, they are reservoirs of those elements; the supply is continually being used to reform new scale to replace that which spalls as a result of thermal cycling or mechanical damage. Thus, by the nature of its protective mechanism, the usable life of a coating is governed by its ability to form the desired protective scale and to retain or replace that scale as needed.

By far the largest use of coatings on superalloys is on components in the hot-gas section of turbine engines, that is, combustors, blades, and vanes. The need for such coatings surfaced in the aircraft engine business in the 1950s when it became apparent that substrate compositional requirements for improved high-temperature strength and optimum high-temperature environmental protection were not

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compatible. Increasing operating temperatures caused excessive oxidation of the high-strength nickel- and cobalt-base superalloys being used for turbine blades and vanes. This led to the development of the simple aluminide diffusion coatings that solved the oxidation problem. Several of these aluminide coatings are still in use today.

Hot corrosion first became a serious problem in those larger industrial and power generation gas turbines that burned low-quality fuels contaminated with sulfur, sodium, and other impurities, or that were located in areas where deleterious species could be ingested through the air intakes, for example, marine or desert environments. The aluminide coatings developed for aircraft engines to solve the oxidation problem were not effective in inhibiting severe hot-corrosion attack. This sparked development of other classes of coatings aimed specifically at combatting hot corrosion. More recently, another distinct mechanism of corrosion, known as low-temperature hot corrosion, was identified. Its successful inhibition has required coating compositions different from those developed for resistance to classical hot corrosion. Thermal barrier coatings (TBCs), which utilize a ceramic layer to reduce the temperature seen by the superalloy component, have been developed to permit substrate materials to be used at engine operating temperatures that might otherwise exceed their capability. Thus, different classes of coating compositions, and processes for applying them, have evolved to meet the differing needs of various applications.

The factors affecting coating selection are numerous. Obviously, environmental protection is the primary reason for using a coating, and this is governed by the design and application of the part. Possible effects of the coating or coating process on the mechanical or thermal properties of the superalloy to be coated must be considered, including the effects of interdiffusion between the coating and the substrate during high-temperature service exposure. Part geometry may govern what coating process is to be used since some application techniques are line-of-sight. Finally, the cost of the coating is always an important consideration and is often the controlling factor in selection.

It is the intent of this chapter to describe the types of coatings and coating processes that have been developed to provide protection for superalloy substrates at high temperatures. The focus will be on the developments of the past 10–15 years, a particularly active period in the history of superalloy coatings development.

COATING PROCESSES

Just about every known method for altering the surface of a metal has been used or considered for the protection of superalloys. In some cases problems with the protection of superalloy components have actually driven the development of new coating processes or the advancement of existing technologies. Superalloy coating processes are often divided into two main categories: those that involve alteration of the substrate outer layer by its contact and interaction with selected chemical species (*diffusion coating processes*) and those that involve deposition of protective metallic species onto the substrate surface, with adhesion provided by a much smaller amount of elemental interdiffusion (*overlay coating processes*).

Diffusion Coatings

Processes in which aluminum is diffused into a surface are the most widely used in the aircraft gas turbine industry. The first methods were slurry-fusion and pack cementation; the latter remains the most widely used process today. Recently, chemical vapor deposition processes have been shown to have advantages for certain applications.

Pack Cementation. In pack cementation, itself a type of vapor deposition process, both the component to be coated and the reactants that combine to form the vapor are contained in the same retort. The reactants, collectively known as the "pack," consist of an aluminum-containing powder (other elements may also be present), a halide that serves as a chemical activator, and an inert filler such as alumina. On heating in an inert atmosphere, the metal powder and activator react to form a vapor that in turn reacts with the surface of the component, enriching it with aluminum. For nickel-base alloys the phases of interest are Ni_3Al, NiAl, and Ni_2Al_3; CoAl and $FeAl_2$ form on cobalt- and iron-base alloys, respectively. The reaction is controlled by the concentrations of the pack constituents and the temperature; these, along with time at temperature and post-coating heat treatment, determine the morphology of the resultant coating.

Diffusion aluminide coatings are classified as either "inward" or "outward" types. An inward coating is produced when the aluminum activity is high with respect to nickel [e.g., high Al and/or activator content in the pack, 1400–1800 °F (760–982 °C) reaction temperature]; the aluminum then diffuses inward faster than the nickel outward through the nickel–aluminum intermetallics that initially form at the surface. When aluminum activity is low with respect to nickel [low pack Al/activator contents, 1800–2000 °F (982–1093 °C) reaction temperature], an outward coating forms; outward diffusion of nickel is favored for subsequent reaction with aluminum in this case. Figure 1 shows typical morphologies of inward and outward

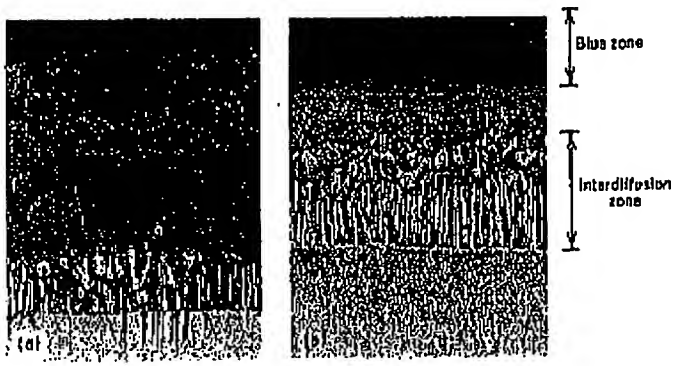

Fig. 1. Microstructures of (a) high-activity (inward) and (b) low-activity (outward) diffusion aluminide coatings on a Ni-base superalloy.[1] 1000×.

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diffusion aluminide coatings.[1] It is interesting to note that both inward and outward coatings may be present on a single component, owing to temperature or composition gradients in the pack or to variable substrate geometry or surface condition.

Both coating types contain the high-melting-point β-NiAl phase. Since NiAl is stable for aluminum contents from about 45 to 60 a/o,[2] pack parameters are often adjusted to produce a more oxidation-resistant hyperstoichiometric NiAl in the outer layer. This "stuffing" of extra aluminum atoms into the NiAl structure causes the usually brown-colored β phase to take on a bluish tint when viewed microscopically. This "blue zone" shows up as a dark layer in Fig. 1b. The solubility in NiAl of most other superalloy substrate elements is small; they are therefore largely rejected from the NiAl outer layer and usually precipitate out as carbides ($M_{23}C_6$, M_6C, MC), metals (e.g., α-Cr), or topologically close-packed phases (e.g., σ, η). Figure 1 shows concentrations of these precipitates in a discrete "interdiffusion zone" between the outer layer and the substrate; in the case of inward coatings precipitates are also present in the NiAl outer layer (Fig. 1a). More detailed discussions on the formation of diffusion aluminide coatings can be found in the first edition of this book[3] and elsewhere.[1]

Because of the compositional complexities of superalloys, a given set of processing conditions will produce different coatings on different substrate alloys. For example, a given coating will usually be thinner on a cobalt-base alloy than on a nickel-base alloy because of the lower diffusivity of aluminum in cobalt. Even when applied to nickel-base superalloys of different compositions, the "same" coating can have different characteristics, particularly with respect to the phase structure of the interdiffusion zone. Single-crystal alloys, for example, generally contain no grain boundary modifiers (C, B, and Zr) because of the absence of grain boundaries. The nature of the interdiffusion zone is altered accordingly; base metal elements present in concentrations that exceed their solubility limits in NiAl must necessarily find means other than carbide formation by which to adapt to the coating phase structure. Parallel alloy/coating development is helpful in generating a desired coating microstructure.

Chemical Vapor Deposition. In the chemical vapor deposition (CVD) process a vapor of predetermined composition, produced independent of the coating step, is introduced into the coating chamber where it reacts with the surface of the part. The major advantage of CVD over pack cementation is its ability to coat serpentine internal cooling passages of film-cooled airfoils. The vapor can be pumped through the internal passages, providing a fairly uniform coating throughout a very complicated geometry. (During pack cementation a small amount of coating vapor does leak into internal passages through cooling holes, but the "throwing power" is extremely limited.) Another advantage of CVD is its compositional flexibility since the thermodynamics of vapor formation are separated from the thermodynamics of the metal-vapor reaction.

Both pack cementation and CVD processes have been used to deposit other elements, such as chromium and silicon, as well as aluminum. Duplex processes,

in which noble metals such as platinum and palladium are plated onto the substrate surface prior to aluminiding, have also been used successfully.

Overlay Coatings

Overlay coatings differ from diffusion coatings in that interdiffusion of the applied surface layer with the substrate is not required to generate the appropriate coating structure or composition. Rather, a prealloyed material having the composition required to form an adherent, protective oxide scale is applied to the surface by any of several methods that require interdiffusion only to ensure that the coating remains attached to the substrate. The overlay coating processes of primary importance today are physical vapor deposition and plasma spraying.

Electron Beam—Physical Vapor Deposition (EBPVD). Physical vapor deposition emerged in the 1960s as the primary overlay coating production technique. The term physical vapor deposition (PVD) refers to deposition of metals by transport of vapor in a vacuum without the need for a chemical reaction.[4] Today, the electron beam (EB) evaporation process is the most commonly used for coating turbine airfoil components. An ingot of the appropriate composition is vaporized in a vacuum using a focused electron beam. The parts to be coated are manipulated within the vapor cloud with the metal condensing out on the preheated substrate surface. The composition of the deposited coating will often be different from that of the starting ingot, due to differences in vapor pressure of the elements in a typical coating alloy; the composition of the ingot must be adjusted accordingly. The technology has progressed to where elements with a broad range of vapor pressures can be simultaneously evaporated from a single source. More detailed descriptions of the process and of the effects of various parameters such as evaporation/deposition rate, substrate preheat temperature, and so on, are presented elsewhere.[5]

Figure 2a shows a typical as-deposited microstructure of a CoCrAlY (Co–19Cr–12Al–0.3Y) coating on a nickel-base superalloy. Post-coating heat treatments

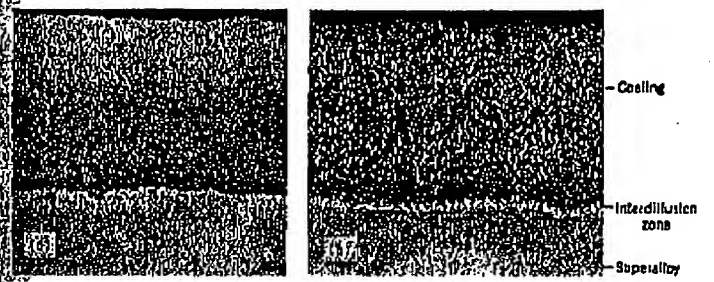

Fig. 2. EBPVD MCrAlY coating (Co–19Cr–12Al–0.3Y) on a Ni-base superalloy substrate (Courtesy of Temescal Division of the BOC Group, Inc.). (a) As coated. (b) After diffusion heat treat. 500×.

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are used to ensure good bonding of the coating to the substrate; the microstructure following heat treatment is shown in Fig. 2b. The high aluminum content of this coating causes the precipitation of β-CoAl in the cobalt solid-solution matrix. Limited interdiffusion does occur during coating and post-coating heat treatment, but the structure and composition of these coatings are essentially constant through the thickness and are changed significantly only within the small interdiffusion zone.

Due to the nature of the deposition process, the structure of the as-deposited coating is typically oriented perpendicular to the substrate surface. Separations between adjacent colonies of deposited coating, known as "leader defects," are often present, particularly on convex curved surfaces. Techniques such as glass-bead peening and laser glazing have been utilized to close these defects in order to prevent premature environmental attack and thermal fatigue cracking.

Plasma Spraying. Plasma spraying has been used as a coating process for many years. The process involves the injection of the coating material, usually in the form of prealloyed powder, into a high-temperature plasma gas stream that has been created inside a plasma gun. Here, the powder particles are melted and accelerated toward the substrate. The molten metal "splats" against the substrate and spreads out in a direction parallel to the substrate surface. The parameters of the process, such as the amount of preheat, plasma gun characteristics, gun to workpiece distance, and so on, all influence the structure and properties of the deposit. For details concerning the plasma spraying process and plasma jet technology, the reader is referred to refs. 6, 7, and 8.

While plasma spray coating is not a new technology, the use of the process in low-pressure vacuum chambers is relatively new. With many of today's coatings being rich in reactive elements such as aluminum and chromium (i.e., MCrAlY), plasma spraying of such coatings in low-pressure environments minimizes the formation of oxide defects within the as-deposited coating structure. The advantages of the low-pressure process also include higher powder particle velocities and broader spray patterns.[9] Coatings can also be applied under the cover of an inert gas shroud. In either case the objective is to deposit a clean, defect-free coating of a desired thickness in a reproducible manner. As with the EBPVD process, adherence of the coating to the substrate is accomplished by means of a post-coat heat treatment.

The microstructure of a typical CoCrAlY plasma sprayed coating is shown in Fig. 3. In the as-coated condition (Fig. 3a) the "splat" interfaces parallel to the substrate surface can be clearly seen. Following diffusion heat treatment (Fig. 3b), individual "splat" layers are no longer visible, and the structure has assumed the two-phase nature that was apparent in the EBPVD coating (Fig. 2b). Typically, the surface finish of plasma-sprayed coatings is rougher than that of EBPVD coatings, and finishing operations (e.g., abrasive slurry and controlled vapor blasting) may be performed to meet the required aerodynamic specifications.

Relative to the EBPVD process, plasma spray offers a significant advantage in terms of compositional flexibility because the vapor pressures of the coating elements are not a concern. Any material that can be produced as a powder of appropriate

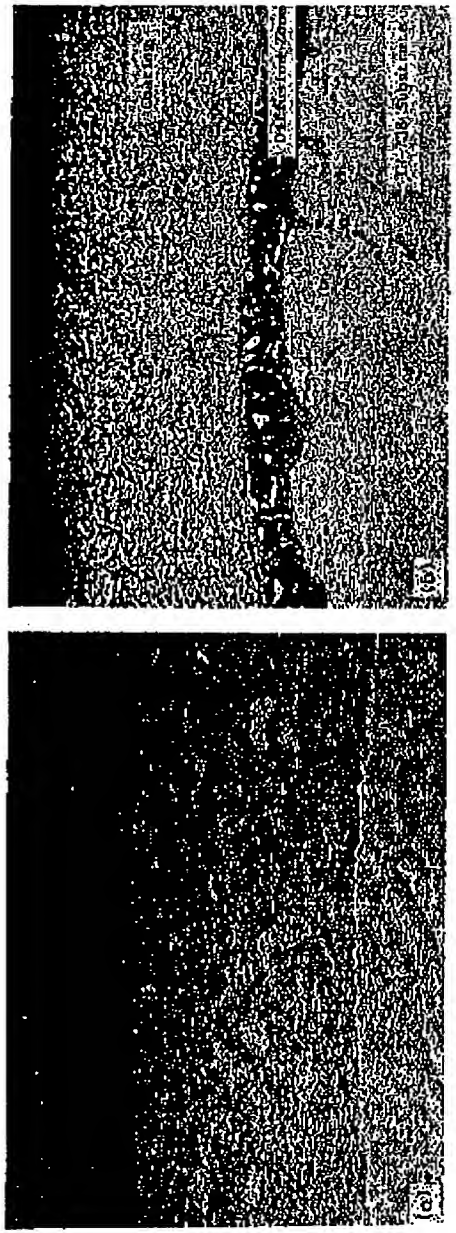

Fig. 3. Low-pressure plasma-sprayed MCrAlY coating (Co–29Cr–6Al–0.3Y) on a Ni-base superalloy substrate. (a) As sprayed; 250×. (b) After diffusion heat treat; 400×.

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size fraction can be sprayed through the plasma gun, although variations in the melting temperature of the starting powder may require modifications to gun design for optimum particle melting.

A major disadvantage of plasma spray and EBPVD relative to diffusion coatings is that they are both line-of-sight processes. With the complex shapes common in turbine blade and vane designs, this limitation inevitably causes problems with coating thickness control due to "shadowing"—the blockage or partial blockage of one part of the component being coated by another part that protrudes into the straight-line path of the coating material being deposited. This problem has largely been overcome by sophisticated manipulation of the part being coated (and of the plasma gun in the case of plasma spraying), although this adds complexity and cost to the process.

The internal passages of film-cooled airfoils cannot be coated using either overlay process, however. A hybrid coating consisting of an overlay coating on the external surfaces and a vapor aluminide on the internal surfaces can be used to provide complete protection in this case. Hybrid coatings constitute an increasingly important part of the superalloy coating business. They are composed of two or more compositions that can be applied by one or more processes. In addition to overcoming the processing limitations of overlay coatings, hybrid coatings can also be used to inhibit undesirable interdiffusion. For example, if the surface of a CoCrAlY coating is enriched with silicon, improved hot-corrosion resistance may be achieved without the deleterious effects of the interdiffusion of silicon with the nickel-base substrate. Also, many turbine blade designs have sufficiently broad temperature profiles so as to permit multiple mechanisms of corrosion to be active during operation. Use of a hybrid coating with layers of differing composition can offer some protection against all mechanisms. A special case of a hybrid coating, the thermal barrier coating, is discussed below.

Miscellaneous Coating Processes

Coatings similar to those formed by pack cementation and CVD have been produced by the spraying or dipping and subsequent high-temperature fusion of metal-containing slurries. Electrophoretic deposition processes have also been used to electrodeposit fine metal particles of the desired composition around complex shapes prior to fusion.[10] Success has been reported in producing MCrAlY overlay coatings by a similar technique called occluded plating.[11]

Controlled composition reaction sintering is a related technique that was developed as a low-cost alternative for applying MCrAlY-type overlay coatings.[12] The MCrY components of the coating are applied by slurry spray, which is followed by a controlled reaction with aluminum and sintering in an aluminide pack of appropriate activity. Success with the reaction sintering approach has been reported with NiCoCrAlY[13] and NiCrSi[14] type coatings.

Sputtering and ion plating fall within the broad definition of physical vapor deposition, but the techniques for producing the vapor cloud differ significantly from EBPVD. In sputtering, a target of the coating material is bombarded by high-energy ions. Target atoms are ejected by momentum transfer and subsequently condense on a substrate positioned in the chamber. Ion plating is a hybrid of sputtering and vacuum evaporation. Prior to evaporation ion bombardment cleans the substrate surface. During evaporation the higher energy of deposition leads to better adhesion of the coating. Sputter ion plating of MCrAlY coatings on turbine blades has been reported and is claimed to be at an advanced stage of development.[15]

In the cladding process the desired alloy composition is fabricated into a thin sheet of the required thickness that is then diffusion bonded onto the substrate surface under high temperature and pressure. Although it has been demonstrated that this process does work,[16,17] the difficulties attendant on fabricating some of the more corrosion-resistant, low-ductility alloys into a thin sheet, make it unlikely that such a process would be used on a large scale. Examples of clad turbine blades with many hours of field service are available.[18]

Surface chemistry modifications can also be achieved by ion implantation and ion beam mixing techniques, which involve the high-energy injection of desired elemental species into a thin surface layer of the substrate.

While all of the techniques mentioned in this section may have achieved important commercial status within some segment of the coating industry, they have not yet become widely established as processes for the coating of superalloy turbine components. Therefore, the following sections of this chapter will concentrate only on those coatings produced by the diffusion aluminide, EBPVD, or plasma spraying process.

COATING EVALUATION

Coatings must be evaluated to ensure that they produce the desired benefits in environmental resistance without unacceptable compromises in the mechanical or physical properties of the coated superalloy. Such tests must be as realistic as possible; in the wrong application or with lack of consideration for a critical parameter, coated part life can be less than uncoated life, even though surface stability may be enhanced. On the other hand, tests that are too severe may overpenalize an otherwise acceptable coating. There is, as usual, a trade-off between the need to test coatings realistically and the cost and duration of those tests.

Since the laboratory tests performed on coatings to determine environmental resistance and effects on substrate mechanical properties are similar to those performed on uncoated superalloys, they will not be discussed in detail here. However, it should be emphasized that the coating and substrate to be used in an intended application must always be considered as a materials system and tested accordingly, since interdiffusion of substrate and coating elements with extended time at temperature can dramatically alter performance.

In addition to the performance testing of coatings, coated components must be evaluated for proper thickness, composition, microstructure, and adherence of the applied coating. This is largely done by destructive optical metallography on coated hardware; considerable effort is currently being expended to identify nondestructive

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techniques such as radiography, ultrasonics, and thermoelectric probe for coating quality assurance.

Although laboratory tests provide extremely useful information about the relative behavior of different coating/substrate systems and, in fact, provide the data required for the design of components using that materials system, it is factory or field engine operation that provides the ultimate test. Such tests include all the variables of stress, strain, temperature, and environment that cannot possibly be duplicated in controlled tests. Long-time exposure of development coatings in the field, in so-called rainbow rotor programs,[18,19] has become particularly useful in sorting out the behavior of various coatings.

COATING PERFORMANCE

Oxidation/High-Temperature Performance

The success of a coating in high-temperature applications as in aircraft engines, is measured by its ability to remain in place, to resist oxidation, and to avoid cracking. In general, the aluminides are most often limited by oxidation behavior, while overlay coatings are more susceptible to thermal fatigue cracking in highly cyclic applications. The major factors that influence the performance of these coatings are described in more detail below.

Aluminide Coatings. Aluminide-coated superalloys oxidize similarly to the more oxidation-resistant superalloys themselves, except that the reservoir of aluminum at the surface is larger. As described in Chapter 11, oxygen combines with aluminum at the surface, and eventually a continuous, protective Al_2O_3 scale is formed. When the scale cracks and spalls due to thermal cycling, aluminum from the coating

Table 1. Results of X-Ray Diffraction Studies on Oxide Scales Scraped from Coated Oxidation Specimens of a Nickel-Base Superalloy

Coating	Time at 2075 °F (1190 °C), h[a]	Estimated Scale Composition (vol. %)			
		Al_2O_3	TiO_2	$NiAl_2O_4$	Other
Aluminide	240	95	5	—	—
	340	60	20	20	—
	→ 790	60	20	20	—
	940	40	10	50	—
	1290	5	5	80	10 NiO
Platinum-aluminide	350	95	5	—	—
	700	80	10	10	—
	→1100	70	15	15	—

[a]Arrow denotes time at which coating penetration was observed based on metallographic evaluation.

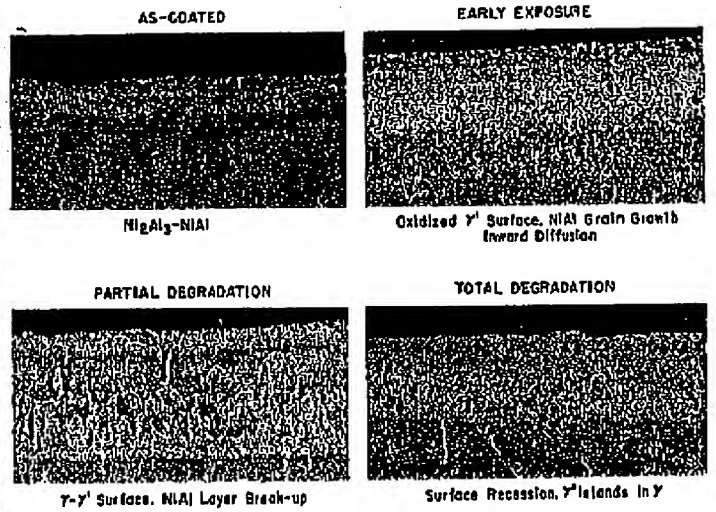

Fig. 4. Decomposition of a high-activity aluminide coating on a Ni-base superalloy.[20] 250×.

diffuses to the surface to reform the protective scale. Throughout the exposure, however, aluminum also diffuses from the coating into the base metal. As aluminum is depleted from the coating by diffusion, β-NiAl converts to γ'-Ni_3Al and eventually to γ-Ni solid solution. When the aluminum level drops to below about 4–5 wt. %, the continuous Al_2O_3 scale can no longer be formed (Table 1), and more rapid oxidation occurs. Figure 4 shows a typical degradation sequence from a microstructural standpoint.

Substrate composition plays a major role in determining coating performance. Table 2 shows the oxidation lives of a typical diffusion aluminide coating on several superalloys. The large differences in life are attributed to substrate aluminum level, which affects the rate at which aluminum will diffuse out of the coating, and to the concentration of certain substrate elements that may enhance (Cr and, to some degree, Hf and Ta) or degrade (Ti, V, W, and Mo) oxidation resistance upon diffusion to the coating surface during post-coat heat treatment and service exposure.

The concentration of refractory elements in the diffusion zone may produce other unusual effects, particularly when thermal fatigue cracking occurs. Normally, the diffusion zone is not directly involved in the oxidation process. If the coating cracks, however, this concentration of refractory elements can be directly exposed to the oxidizing environment and may oxidize rapidly. This condition can be reproduced by introducing cracks into oxidation specimens prior to testing. For an experimental vanadium-containing substrate alloy, coating life dropped precipitously when such cracks were introduced; a concentration of vanadium in the diffusion zone of the

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Table 2. Oxidation Lives of Diffusion Aluminide Coating (CODEP) on Several Superalloys

Alloy	Coating Life at 2075 °F (1190 °C), h[a]
X-40	23
CMSX-3	85
René 80	100
René 125	300

[a] Mach 1.0 gas velocity, air, cycled once per hour; life determined by visual and metallographic assessment of coating penetration.

coated alloy, while inconsequential in the normal oxidation process, resulted in catastrophic oxidation when the coating was cracked (Fig. 5a). Figure 5b shows this ballooning or burrowing oxidation as it occurred on an aluminide-coated vane from a field-tested aircraft engine. This effect must be considered when selecting coatings for highly cyclic applications.

Another important aspect of the high-temperature performance of diffusion aluminide coatings that is related to the nature of the interdiffusion zone is the temperature at which incipient melting occurs. Even though the melting point of NiAl is around 2900 °F (1593 °C) and that of most superalloys greater than 2300 °F (1260 °C), incipient melting has been observed in the diffusion zone of aluminide-coated superalloys at temperatures as low as 2050 °F (1121 °C).[11] On a macroscopic scale, this can result in wrinkling and, in severe cases, peeling of the coating before oxidation penetration occurs. Again, owing to differences in the nature of the phases in the diffusion zone, the temperature at which melting occurs varies for the same coating on different alloys.

Overlay Coatings. The oxidation scenario for overlay coatings is basically the same as that for diffusion aluminide coatings. The presence of chromium and active elements such as yttrium improve oxidation resistance by increasing the activity of

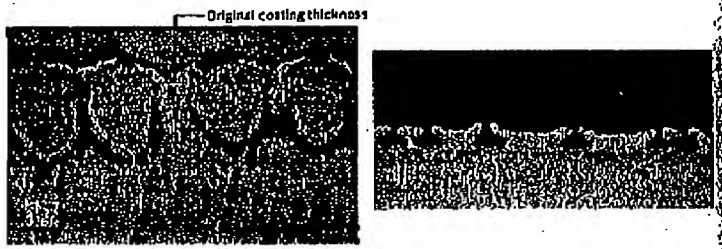

Fig. 5. Ballooning oxidation in the interdiffusion zone of a diffusion aluminide–coated Ni-base superalloy. (a) Precracked oxidation test specimens after exposure; 100×. (b) Field-tested turbine vane; 50×.

Table 3. Oxidation Resistance of Coatings on a Nickel-Base Superalloy

Coating	Coating Life at 2075 °F (1190 °C), h[a]
Aluminide	100
Platinum-aluminide	250
NiCoCrAlY	>1000

[a] Mach 1.0 gas velocity, air, cycled once per hour; life determined by visual and metallographic assessment of coating penetration.

aluminum and by improving the spallation resistance of the Al_2O_3 scale, respectively (see Chapter 11). Thus, MCrAlY coatings have been designed that significantly outperform diffusion aluminides in oxidation tests (Table 3). NiCoCrAlY compositions are the most widely used for oxidation protection; the addition of cobalt to the basic NiCrAlY composition, while affording some improved environmental resistance, was also found to improve coating ductility.[21]

As a NiCoCrAlY coating oxidizes, grains of the aluminum-rich β phase gradually convert to islands of γ′; eventually only the less-resistant γ matrix phase remains (Fig. 6). Originally, it was thought that overlay coating composition and performance would be independent of substrate composition. This is not totally accurate, particularly in high-temperature applications where diffusion rates are high. The large grain boundary area present in fine-grained overlay coatings affords a large network of diffusion paths for base metal elements, which can be present in small amounts in the as-deposited and diffusion heat-treated coating (Fig. 7a). With exposure, the amounts of these elements at the coating surface increase (Fig. 7b). As shown in Table 4 and elsewhere,[21] the oxidation resistance of an overlay coating can indeed be affected by substrate composition, just as are the diffusion aluminides.

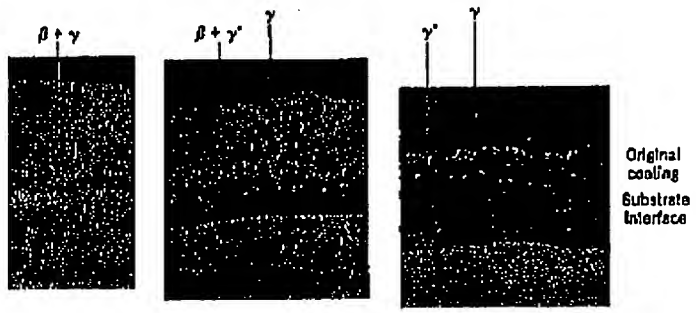

Fig. 6. Typical microstructural changes in a NiCoCrAlX coating on a Ni-base superalloy exposed in a cyclic oxidation test at 2075 °F (1135 °C), air, Mach 0.05 gas velocity, 1 cycle/h. (a) As coated. (b) Exposed 150 h. (c) Exposed 450 h. 250×.

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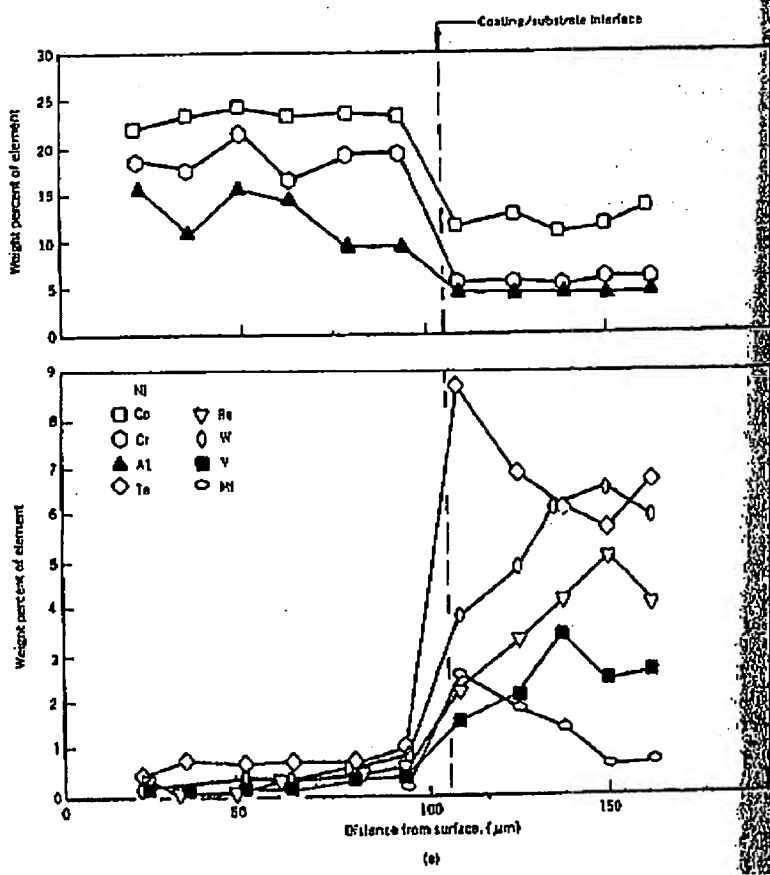

Fig. 7. Electron microprobe traces across a NiCoCrAlY coating on a Ni-base superalloy before and after high-temperature exposure: (a) as coated and diffusion heat treated.

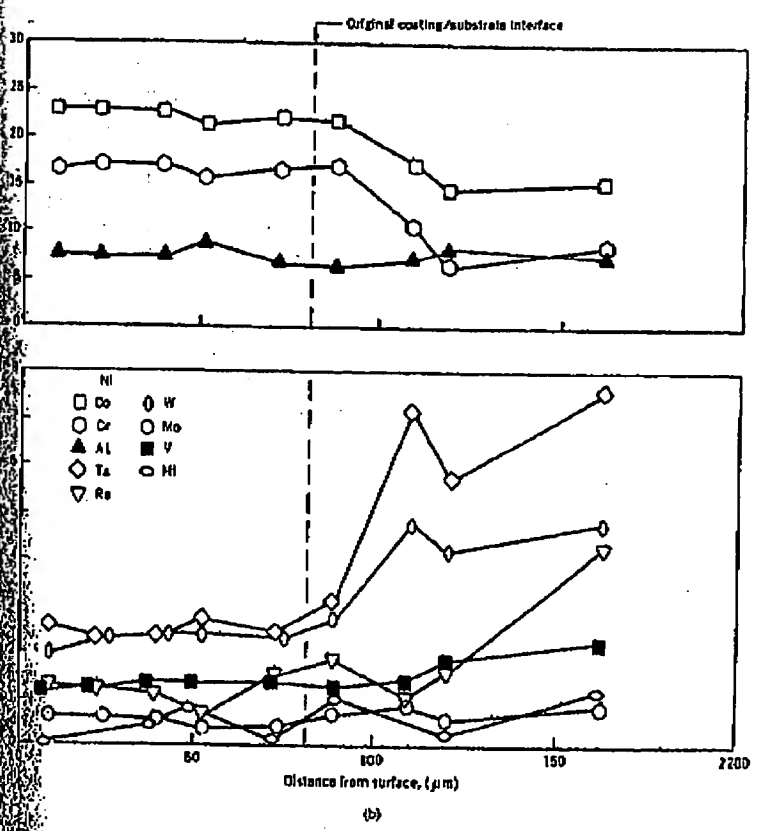

Fig. 7. *(Continued)* (b) after 750 h, 2075 °F (1135 °C), cyclic air exposure.

In addition to superior oxidation resistance, a major advantage of MCrAlY coatings over diffusion aluminides for high-temperature applications is a high melting point that is essentially independent of substrate influence. Melting does not occur in the interdiffusion zone at temperatures significantly lower than the melting point of the bulk overlay composition. Compared to incipient melting points of 2050–2200 °F (1121–1204 °C) for most diffusion aluminides, overlay coatings have survived exposures of 2350 °F (1288 °C) with no evidence of melting. However, the high melting points of the overlay coatings must be balanced against their

strengths at high temperatures, which can result in thermal fatigue cracking in cyclic applications.

MCrAlY overlay coating development has largely focused on elemental additions to improve oxidation resistance. Modified NiCoCrAlY containing silicon, tantalum, and platinum, for example, has exhibited improved resistance to oxidation, though ductility is usually reduced.[23] Coating compositions are now being developed that limit diffusion between the coating and substrate and increase the high-temperature strength of the coating in order to improve thermal fatigue resistance. The improved understanding, currently being developed, of the strain–temperature cycles experienced by superalloys and coatings in thin-walled, internally cooled turbine airfoil config-

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Table 4. Oxidation Resistance of NiCoCrAlY Coating on Various Superalloy Substrates

Substrate	Coating Life at 2075 °F (1190 °C), h[a]
René 80	125
MM-200	200
Advanced Ni-base alloy	500

[a] Mach 1.0 gas velocity, air, cycled once per hour; life determined by visual and metallographic assessment of coating penetration.

urations will also provide direction for future overlay coating development. The almost unlimited compositional flexibility afforded by the low-pressure plasma spray process will continue to provide opportunities for tailoring an overlay coating composition to provide optimum performance on a particular substrate alloy in a service application of interest.

Hot-Corrosion Performance

The need for hot-corrosion-resistant coatings exists in the marine and industrial gas turbines. Here, the thermal cycles are generally not as severe as those in aircraft applications, and thus the limitations on overlay coating use may not be as strict. Often, the potential for hot corrosion can be reduced by proper fuel cleanup and adequate air filtration, but coatings are still required to prevent catastrophic corrosion failure in the event such systems are not available or not performing properly.

Diffusion Coatings. Use of the simple aluminide diffusion coatings in applications where hot corrosion was the primary problem generally led to unsatisfactory results unless the corrosion conditions were relatively mild.[24] Commercial availability of the platinum-aluminide coatings in the early 1970s[25] provided a marked improvement in the hot-corrosion resistance of the aluminide coatings. Other precious metal aluminides, which utilize less expensive elements such as rhodium or palladium in place of platinum, have been developed, but in general, they do not have the capability of the platinum-bearing versions. However, cost considerations can make these coatings, as well as various silicide and duplex chromium–aluminum diffusion coatings, more attractive for use in less severe environments.

The mechanism by which platinum enhances the corrosion resistance of aluminide coatings is not clearly understood. Platinum does not participate directly in scale formation. Rather, it appears to increase the activity of aluminum at the surface and/or influence scale adherence or the rate of scale formation. Degradation of the platinum–aluminide coatings occurs with the depletion of aluminum available to form the protective scale. As was discussed in Chapter 12, the presence of molten alkali metal salts can hasten the destruction of the alumina scale and thus accelerate the consumption of aluminum. A $PtAl_2$ phase (if it is present initially) goes into solution as aluminum is utilized in scale formation. Eventually, as sufficient aluminum

is consumed, the β matrix phase is transformed to γ′, and effective corrosion protection ceases. In the advanced stages of attack the formation of chromium-rich internal sulfides in the substrate or the interdiffusion zone between the substrate and coating indicates that the usable life of the coating has been exceeded. Micrographs illustrating the different stages of this degradation process are shown in Fig. 8.

The platinum–aluminide coatings are somewhat less ductile than the simple aluminides and therefore may be more restricted in their use in some aircraft engines with severe cyclic operating patterns. However, service experience has generally been very favorable for both land-based and aircraft applications. Satisfactory performance to 40,000 h and beyond has been reported for land-based turbines operating in corrosive environments that would cause the destruction of uncoated superalloys in relatively short times.[18]

Overlay Coatings. Several MCrAlX overlay coatings have also been shown to possess excellent hot-corrosion resistance, both in burner rig testing and in field service.[26,18] The best of the MCrAlX coatings for severe hot-corrosion environments are cobalt based with relatively high chromium–aluminum ratios. The nickel- (or NiCo) and iron-base coatings are effective in oxidation and in relatively mild hot-corrosion environments. A good hot-corrosion MCrAlY coating is exemplified by the Co–29Cr–6Al–0.3Y composition, which is an alumina former despite its relatively high chromium level. Generally, as the chromium–aluminum ratio increases, the hot-corrosion resistance increases at the expense of some oxidation resistance. Whether or not the active element addition (i.e., Y and/or Hf) is as effective in hot corrosion as it is in oxidation is not clearly established, but since many applications on turbine airfoils inevitably involve oxidation as well as hot corrosion, overlay coatings developed for hot-corrosion resistance usually contain an active element.

Other approaches to developing hot-corrosion-resistant overlay coatings have included the use of silicon as either an outer layer in a duplex or graded composition[27] or as the main scale-forming ingredient in a NiCrSi type of coating.[28] The use of noble metals such as platinum in CoCrAlXs has been reported to produce excellent hot-corrosion resistance in marine environments.[29] In general, it would appear that the most effective hot-corrosion-resistant overlay coatings are those alumina formers in which chromium has been increased to the maximum level consistent with the desired mechanical properties, and to which elements such as yttrium, silicon, platinum, and hafnium have been added for optimized performance in a given environment or with a given substrate.

The degradation of MCrAlY coatings in hot corrosion is characterized by the presence of internal sulfides as well as oxides within the coating (Fig. 9). Typically, these chromium-rich sulfides precede the internal oxides, much as in the attack of bare superalloy. Ultimately, however, it is the depletion of the aluminum, as well as the chromium, needed to form the protective scale that leads to coating failure. Field experience with some early-generation MCrAlY coatings has shown long-time performance at least equivalent to that of the platinum–aluminide coatings in terms of rate of attack.[18] Given the increased coating thicknesses possible with the overlay coating processes, improved corrosion life of the coated part can be achieved.

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Fig. 8. Pt–Al coating degradation in a hot-corrosion environment. (a) As coated. Note surface layer containing light-colored $PtAl_2$ phase. (b) Approximately 10,000 h field service in low-corrosion-potential environment. $PtAl_2$ phase has been solutioned, leaving gray β-NiAl phase with minor surface scaling. (c) Approximately 10,000 h field service in a relatively severe hot-corrosion environment. Gray β-NiAl phase has converted to light-colored γ-Ni-Al or perhaps γ-Ni solid solution. Fine gray sulfides are present in light outer layer, but attack has not penetrated through diffusion zone into substrate. 500×.

Fig. 9. MCrAlY overlay coating degradation in hot-corrosion environment. (a) Approximately 28,000 h field service in low-corrosion-potential environment. Coating shows internal oxidation with small β-depletion layer but very few, if any, sulfides. (b) Approximately 1,000 h in severe hot-corrosion laboratory test environment at 1600 °F (871 °C). Coating shows heavy external scaling, complete β-phase depletion, internal oxides (large dark-gray islands), and internal sulfides (lighter gray particles) in both coating and diffusion zone. 400×.

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The use of MCrAlX overlay coatings may therefore prove to be more cost-effective, particularly in those hot-corrosion applications where thermal cycling is not overly severe.

Low-Temperature Corrosion Performance

Experience has shown that chromia and possibly silica scales, rather than alumina scales, are required for optimum protection against low-temperature hot corrosion. Since most of the coatings developed for hot-corrosion and oxidation protection depend on alumina scales, these have generally proven ineffective in combatting low-temperature corrosion.[26] Therefore, this section will include discussion of those chromia- or silica-forming coatings that have most recently been utilized for low-temperature corrosion protection.

Diffusion Coatings. Several commercially available chromide diffusion coatings have proven to be effective against low-temperature corrosion. The ability to rapidly form a continuous, adherent Cr_2O_3 scale appears to be the main requirement for protectiveness. Most pack diffusion chromide coatings are relatively thin [1.5–2.0 mils (0.038–0.051 mm) at most] due to the limitations of the process. Fortunately, the amount of interdiffusion that occurs in a lower temperature environment is small; coating thickness is less of a concern than at higher temperatures where protective elements can be rapidly lost to the substrate. A thinner coating is also more desirable from a mechanical property standpoint, since high chromium compositions tend to be less ductile and therefore more prone to cracking.

Simple silicide diffusion coatings, while probably very effective in combatting low-temperature hot corrosion due to the formation of a SiO_2 scale, are not used in turbine engines because of the deleterious effects of silicon interdiffusion with nickel-base superalloys. The use of more complex silicides (e.g., a Ti–Si composition[30] or Si-rich outer layers in duplex or graded coatings) are the preferred ways of utilizing silicon in the coating of superalloys.

Overlay Coatings. Overlay coatings with relatively high chromium contents (> 30 wt. %), including MCrXs (see ref. 31) and MCrAlYs (ref. 32), have been reported in the literature; all are predominantly chromia formers. High-chromium cobalt-, nickel-, and iron-base coatings are all effective against low-temperature hot corrosion. However, since the temperature range encountered in many turbine airfoil applications will require protection against both mechanisms of corrosion, the use of cobalt-base coatings with high chromium levels is preferred.[26]

The microstructure of a typical high-chromium CoCrX plasma-sprayed coating is similar to that of the CoCrAlY shown earlier (Fig. 3b) except that the second phase is a cobalt–chromium σ phase rather than the β CoAl phase. Its burner rig test performance relative to that of a more "standard" CoCrAlY coating (i.e., Cr level less than 30 wt. %) is shown in Fig. 10. Clearly, the higher chromium CoCrX coating has vastly superior resistance to low-temperature pitting corrosion in this test. Some investigators[31] have indicated that aluminum may detract from the ability

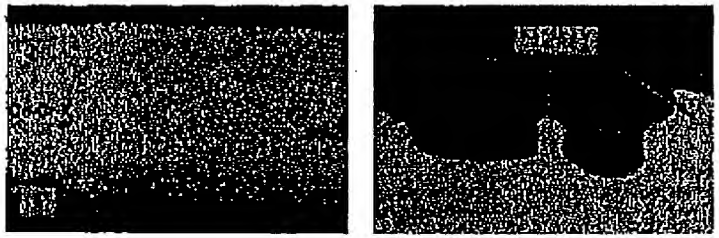

Fig. 10. Typical coating degradation observed on two overlay coatings, CoCrX (> 40 wt. % Cr) versus CoCrAlY (<30 wt. % Cr) in low-temperature hot-corrosion burner rig testing at 1350 °F (732 °C). Fuel: diesel oil + 1% S + 125 ppm Na as sea salt + 784 cm³/min SO_2; air/fuel = 60, 1 atm, gas velocity = 70 ft/s. (a) CoCrX (>40% Cr), 1021 h, 250×. (b) CoCrAlY (<10% Cr), 64 h, 100×.

of such coatings to resist low-temperature corrosion, while others have found high-chromium CoCrAlY coatings to be acceptable for certain applications.[32] This apparent contradication may reflect differences in the expected environment and thus the test parameters. Suffice it to say that low-temperature corrosion resistance is promoted by the presence of chromia or silica scales, with the alumina-forming coatings that have been developed for hot corrosion and oxidation being less appropriate for this purpose.

Many newly developed low-temperature corrosion coatings are now undergoing field tests, with the results to be reported in the next few years. The identification of low-temperature corrosion as a separate mode of attack, and the coating development work spawned by that realization, is recent enough that as of this writing the record of field performance has still to be written.

THERMAL BARRIER COATINGS

Thermal barrier coatings represent perhaps the most promising and exciting development in superalloy coatings research in recent years. Given the driving force to increase the efficiency and/or output of gas turbines (which inevitably means an increase in turbine inlet temperature), any mechanism by which temperature limits can be raised by overcoming hot-section material restraints is of significant interest. Thermal barrier coatings offer this potential.

Description

A thermal barrier coating, or TBC, is a multilayer coating system that consists of an insulating ceramic outer layer (top coat) and a metallic inner layer (bond coat) between the ceramic and the substrate. In most cases the top coat and bond coat are applied by plasma spraying; sputtering and EBPVD have also been used. Typically, the ceramic top coat is 5–15 mils (0.127–0.381 mm) thick while the metallic bond

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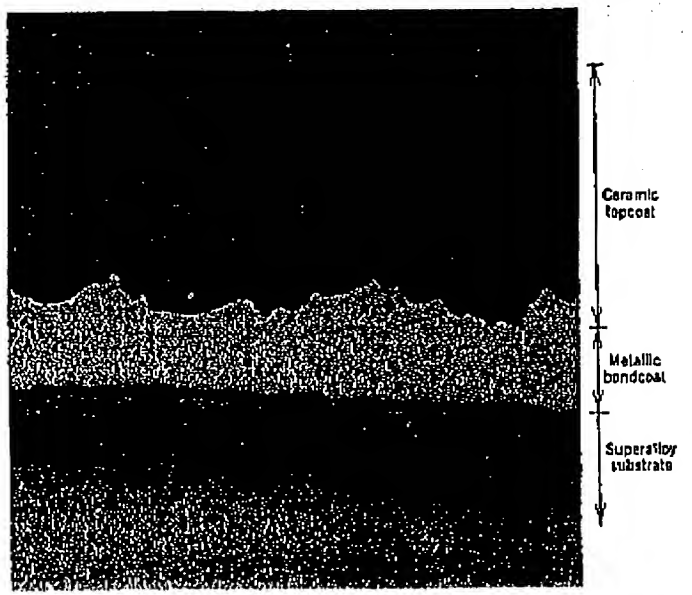

Fig. 11. Microstructure of typical thermal barrier coating on Ni-base superalloy substrate. 200×.

coat is 3–5 mils (0.076–0.127 mm) thick. The microstructure of a typical system is shown in Fig. 11.

The function of the ceramic layer is to insulate the metallic substrate from higher surface temperatures than it might otherwise be able to tolerate. Depending on the thermal conductivity of the ceramic, coating thickness, and the heat flux created by the design and cooling configuration of the particular component, temperature gradients of several hundred degrees can be created through the coating. Zirconium oxide (ZrO_2) has been the material of choice because of its very low thermal conductivity and its relatively high (for ceramics) coefficient of thermal expansion. When heated to above about 2140 °F (1170 °C), however, the ZrO_2 structure changes from monoclinic to tetragonal; the accompanying volume change of 4–6% can result in severe spalling of the ceramic layer. Stabilization of the tetragonal phase to room temperature or below can be accomplished by the addition of MgO, CaO, Y_2O_3, or other rare-earth oxides to the ZrO_2. Typical state-of-the-art TBCs utilize ZrO_2 partially stabilized with 6–8 wt. % Y_2O_3.

While the zirconia top coat provides an excellent barrier to heat, it is a sieve with respect to oxygen transport. A major function of the metallic bond coat is thus to impart environmental resistance to the substrate, since the gross formation of oxides at the metal–ceramic interface can cause spallation of the ceramic. The roughness of a bond coat applied by plasma spraying aids in adhesion of the plasma-

sprayed ceramic top coat by providing some mechanical interlocking. Air plasma-sprayed MCrAlY's were originally used for most TBCs; low-pressure plasma spray is also used today. An excellent summary of recent literature related to TBCs can be found elsewhere.[33]

Performance/Reliability

By their nature, metal oxides are relatively strain-intolerant. Unfortunately, sources of strain abound in TBCs, resulting from residual stresses from the coating process, thermal expansion mismatch between the ceramic and metal layers, oxidation/corrosion of the bond coat, phase transformations in the ceramic layer caused by thermal cycling, and thermal gradients typical of hot-section components in service. Some components also see mechanically induced strains. Consequently, the ceramic layer is prone to spalling which most often occurs just adjacent to its interface with the bond coat.[34]

In response, much recent work has focused on processing techniques that produce a more strain-tolerant ceramic structure and on the development of bond coats with improved environmental resistance, mechanical properties, and metallurgical stability. Approaches for the development of more strain-tolerant structures have included closer control of the as-deposited phase structure and the intentional incorporation of defects during processing. The as-deposited phase structure, which is critical to the performance of the top coat, has been shown to be very sensitive to the composition and structure of the starting powder[35] as well as to variations of plasma spray parameters (substrate temperature, gun-to-workpiece distance, etc.). The introduction of defects into the ceramic layer has been accomplished by careful control of these parameters in order to produce a controlled amount of porosity and/or microcracking in the deposit.[36] Post-deposition processing, including annealing and quenching, has also met with some success in producing the desired defect structures.[37]

Sputtering[38] and EBPVD[5] have been used to produce segmented structures consisting of a number of fine cracks perpendicular to the substrate surface. This division of the ceramic layer into a network of small individual segments is thought to improve its strain tolerance; improved cyclic lives have been reported for such structures.

Use of improved oxidation- and corrosion-resistant bond coats also leads to improved performance, as do bond coats applied in protective environments. As an aid to protection of the bond coat, techniques such as laser glazing of the ceramic or adjustment of plasma spray parameters near the end of the coating process have been used to produce a dense surface layer that precludes the absorption of corrosive salts.[39]

Current Applications

Commerical application of TBCs in turbine engines has thus far been restricted primarily to the stationary components of the combustion and exhaust systems (e.g., burner cans and transition pieces). Significant reductions in metal substrate temperatures have been achieved, leading to the elimination of creep deflection problems in those

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